INVESTIGATION OF PHASE AND EMULSION BEHAVIOR, SURFACTANT RETENTION, AND CONDENSATE RECOVERY FOR CONDENSATE/WATER/ETHANOL MIXTURES

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DISCLAIMER

Investigation of Phase and Emulsion Behavior, Surfactant Retention, and Condensate Recovery for Condensate/Water/Ethanol Mixtures

ABSTRACT

This semi-annual technical progress report describes work performed at Morehouse College under DOE Grant No. DE-FG26-02NT15447 during the period October 01, 2003 to March 31, 2004 which covers the third six months of the project. Presently work is in progress to characterize phase and emulsion behavior for ethylbenzene/water/ethanol system. Ethylbenzene that has the equivalent carbon number is used as the model condensate. During this reporting period, temperature scans were performed mixing equal volumes of ehtylbenzene and 10mM NaCl water with various concentrations of ethanol ranging from 2 to 70 vol%. For the range of temperatures tested (2 to 70 °C), results indicate that temperature is invariant and produced a single phase for ethanol concentrations greater than 60 vol%. For ethanol concentrations less than 60 vol%, only two phases were obtained with aqueous rich bottom phase more in volume than that of the ethylbenzene rich top phase. Linear coreflooding experiments were completed by our industrial partner in this project, Surtek, CO, to measure the condensate recovery in flooding processes. It was found about 30% ethylbenzene recovery was obtained by the waterflooding, however, 2wt% ethanol flooding did not produce incremental recovery of the ethylbenzene. Radial coreflooding with ethanol injection prior to water injection is in progress to assess the effectiveness of the surfactant flooding in the recovery of condensate.

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INTRODUCTION

The Department of Energy has been sponsoring fundamental and applied research in the natural gas recovery area. Recently, NPTO/Tulsa has been interested in research focussing on innovative methods for technologies towards improved gas and condensate recovery. If an effective method can be found, the potential for incremental recovery is great.

The major factors causing hydrocarbon losses in a reservoir during production of gas and gas condensate fields are related to pressure depletion, retrograde condensation, and water encroachment. The most widespread and simple method of producing gas and gas condensate fields is by depletion, utilizing the natural reservoir pressure only. The major disadvantage of the method is the low condensate recovery. The ultimate condensate recovery from gas condensate fields is 30 - 60 %, depending on the initial content of condensate in gas. In comparison, the final recovery of gas in dry gas fields can be up to 95 %. Despite the low recovery of condensate associated with natural depletion, this method is still widely used in the majority of gas condensate fields in the world. The reasons for this are both technological and economic. Achieving increased production in partially depleted gas and gas condensate fields is essential for many gas producing companies. Incremental production can be very profitable especially in industrially developed countries. Worldwide, the potential for production and improved recovery from gas condensate fields is considerable. In order to improve the recovery from gas condensate fields innovative methods are required.

Depletion of reservoir pressure leads to a reduction in flow capacity and normally causes retrograde condensation. Offsetting the reduced flow capacity by lowering the bottom hole flowing pressure can result in near wellbore retrograde condensation, which leads to decreased effective permeability and additional reduction of flow rates. Lower production rates leads to earlier abandonment resulting in lower ultimate recovery. Significant amounts of condensate can accumulate in the near wellbore zone due to the large pressure drop in this zone. This condensation takes place in addition to the condensation within the reservoir caused by the general pressure depletion. As a result of this condensate accumulation, liquid saturations in the near wellbore zone can considerably exceed the average value over the reservoir as a whole. This causes a large reduction in well productivity. The reduction of well productivity caused by near wellbore accumulation of retrograde condensate has been observed at many fields in the USA, Russia, and Canada. At these fields the well productivity decrease reached 50% in some productive intervals due to condensate accumulation. Further pressure reduction down to the pressure of maximum condensation results in increased volume of condensed liquid. Then the mixture enters a range of direct evaporation and will result in further decrease of pressure. Pressure depletion below the dew-point pressure causes retrograde condensation throughout the entire system that leads to greater than 50% reduction in well productivity.

Water encroachment into a gas or gas condensate reservoir has two opposite effects: 1)maintenance of reservoir pressure, and 2)trapping gas and condensate behind the water level at higher pressure than by depletion and thus reduceing the recoverable reserves. Selective water encroachment in a reservoir and breakthrough of water to production wells result in an accumulation

of water in wells and their premature shut-in at higher formation pressures. The impact of each of the above mentioned factors on production and ultimate recovery of condensate and gas varies from reservoir to reservoir, but water encroachment is observed at all gas condensate fields to a certain degree. Application of surfactant flooding technology that is used in the Enhanced Oil Recovery technology may hold great potential for the improved recovery of condensate from the water encroached gas and condensate fields. For this, a research project aimed at understanding the emulsions formed by water, condensate, and a cosurfactant such as ethanol would provide valuable information including how to reduce the interfacial tension between encroaching water and condensate, and under what conditions and how this can be used towards improved recovery. The use of ethanol as the surfactant in this project would also provide valuable information on how to remove the condensate from near the wellbore by reducing the interfacial tension between the gas and condensate and hence improve the gas flow from condensate accumulated wellbores.

Application of surfactants and hence formation of emulsions depend on the desired morphology, for example, a "condensate -in-water" or a "water-in-condensate" emulsion. Formation of the "wrong" morphology or inversion from the desired morphology to the "wrong" morphology causes the product or process to fail. Mixtures of water, condensates, amphiphiles, and salt may separate into three coexisting liquid phases within a well defined temperature interval, the mean temperature of which depends sensitively but systematically on the nature of the condensate and the amphiphile and on the salt concentration. At the mean temperature of this interval one finds--for thermodynamic reasons--a maximum of the mutual solubility between water and condensate and a minimum of the interfacial tension between the aqueous and the condensate-rich phase. Both of these properties are of considerable interest for both research and industrial application.

Many, if not most, of the two-phase emulsions that may commonly exist at various temperatures in systems of surfactant, condensate, and water form in systems that also can form [1] triconjugate condensate-rich top phase (T), water-rich bottom phase (B), and middle-phase microemulsion (M). For such systems, two-phase emulsions may form in any of the various two-phase regions [2-3] that surround a stack of tie triangles in the triangular-prismatic phase diagram. For temperatures between Tlc and Tuc--the range over which phases T, M, and B coexist--there are three two-phase regions and thus six nonmultiple, two phase emulsion morphologies [4]. For such systems the plotting of phase boundaries and of boundaries between different emulsion morphologies in accordance with the phase rule introduces a rigorous way of showing how the occurrence of each of the six two-phase morphologies depends on temperature and composition. For the limiting tie lines (i.e., the sides of the tie triangle), where the three-phase and two-phase regions meet, the six two-phase morphologies will be formed by the triconjugate phases taken pairwise: T/M, M/T; B/T, T/B; and M/B, B/M [5].

One of the most widely observed phenomena of emulsion inversion is inversion hysteresis [6]. For example, the phase volume fractions at which the inversions A/B to B/A and B/A to A/B occur are somewhat different. If the pair of phase volume fraction points at which the pair of conjugate inversions occur are measured at different temperatures, the resulting measurements form a pair of inversion hysteresis lines in phase volume fraction-temperature space. The fractional phase volume

at which inversion occurs is believed to depend on many different factors, such as the temperature, structure and concentration of the emulsifying amphiphile, salinity, and hydrocarbon composition. The factors that control dispersion morphology and inversion are now well understood [5]. Qualitatively, dispersion inversion has long seemed to be a catastrophic event. The properties of an A/B (A-in-B) dispersion are very different from the properties of a B/A (B-in-A) dispersion, and the inversion from one morphology to the other is often abrupt and irreversible. Inversion is marked by a sudden change in the physical properties (e.g., electrical conductivity) of the dispersion, indicating an abrupt change in the structure of the dispersion [5]. Smith et al. [5,7-10] demonstrated for several oil/water/surfactant systems that elementary catastrophe theory provides a unifying framework to explain these phenomena in systems of variable oil/water ratio and amphiphile concentration at constant temperature and pressure. Smith et al. [1] hypothesized that wherever a phase critical point occurs, there will be a "critical point" for dispersion inversion, also; that is, pairs of dispersion inversion hysteresis lines meet at a point, and this point coincides with the critical point for the two phases of the dispersion.

Sampath et al. [5] determined the morphologies and phase volume fractions at which inversion occurred for (macro)emulsions formed by the middle-phase microemulsion (M) and water-rich bottom phase (B) by means of electrical conductivity measurements for the chemical system C6H13(OC2H4)2OH/n-tetradecane/aqueous 10mM NaCl at temperatures from 25 EC down to 12 EC, near the lower critical end-point temperature (Tlc = 10.4 EC). The M/B and B/M morphologies and their inversion hysteresis lines were found to conform to the previously postulated dispersion morphology diagram; that is, within experimental uncertainties, the two emulsion inversion lines in phase volume-temperature space met at a "critical point"' that coincided with the lower critical end point for the phases.

The phase behavior, interfacial tension and solution physical parameters only define a single interface in the condensate recovery process, the water-condensate interface. In a condensate and water filled reservoir system, two other interfaces exist, the condensate-rock and water-rock interface. The effect of these two interfaces on the condensate recovery process are just as important, if not more important, than the water-condensate interface [11-14]. Linear and radial corefloods are used to test the effect of the two rock interfaces on the condensate recovery potential of the surfactant systems. Linear corefloods provide adsorption coefficients of chemical onto the rock surface and define fluid rheology as the ability of the solution to flow through porous media. Radial corefloods to estimate condensate recovery potential are preferable to linear corefloods for a number of reasons [11-16]. The pore volume of a radial core is greater than that of a linear core making measurement of the injected and produced fluids volumes more accurate. The flow patterns in a radial core allow expansion of the interface between the injected surfactant and the fluid in the core to occur in a similar manner as in a vertical well in the field. When fractional pore volumes of chemical are injected, chemical banks thin in a manner analogous to a vertical well in the field allowing dispersion, dilution, and other potentially deleterious effects to occur. Recently, Moeti, Sampath, Smith, and Pitts [17-19] investigated the suitability of hybrid (ionic and nonionic) surfactants for enhanced oil recovery and observed inversion hystereses but lower surfactant and hydrocarbon recovery for these surfactants.

To this end, applying our experimental and modeling capabilities in the emulsion research [5,17-19], this project seeks to characterize the phase and morphology behavior of ethylbenzene that has the equivalent carbon number of condensate when mixed with water and a cosurfactant such as ethanol and develop a database for use in improved condensate recovery from water encroached wells. Detailed information on optimal salinity, temperature, emulsion morphologies including inversion hystereses, lower and upper critical points, and recovery efficiency will be obtained for ready use in actual field operations. The information to be obtained will also be useful in evaluating the use of ethanol as the surfactant to remove the condensate from near the wellbore to improve the gas flow in condensate accumulated wellbores.

The specific objectives are:

1) Perform salinity and temperature scans to obtain optimal salinity and temperature at which all phases coexist.

2) Perform emulsion morphology and coreflooding experiments for the ethylbenzene/water/ethanol system that gives the best results in objective 1.

Experiments and analyses are being carried out to meet the project objectives. Objectives 1 and emulsion measurements are being accomplished by Morehouse. Coreflooding experiments are being accomplished by Surtek, our industrial partner in this project. The successful accomplishment of the objectives will improve our knowledge towards improved condensate recovery from water encroached wells.

EXECUTIVE SUMMARY

In this semi-annual report, the work performed under DOE Grant No. DE-FG26-02NT15447 during the period October 01, 2003 to March 31, 2004 which covers the third six months of the project is described and the major accomplishments are highlighted summarizing the most important research results.

Many surfactants will simultaneously form multiple coexisting liquid phases when mixed with condensate and water within a well defined salinity and temperature interval. At the mean temperature of this interval one finds--for thermodynamic reasons--a maximum of the mutual solubility between water and condensate. In a three phase mixture, the middle phase, which contains the greatest concentration of surfactant, is called a microemulsion. Typically the microemulsion reduces the interfacial tension between hydrocarbon and water by about three or four orders of magnitude. These ultralow tensions allow the hydrocarbon-rich (top) phase to be pushed through porous media by the aqueous (bottom) phase, and the three liquid phases flow as macroemulsions. The microemulsion phase can also form two-phase, or three-phase, macroemulsion structures or morphologies when mixed with either one, or both, of the other two phases, depending on the temperature, relative volumes of the phases, and other factors. Formation of a wrong morphology or inversion from the desired morphology to the wrong morphology is also possible. Investigation of these morphologies, when they occur, and their flow through porous media are of considerable interest for both research and industrial application.

This project seeks to characterize phase and emulsion behavior, and condensate recovery for condensate/water/ethanol systems. The successful accomplishment of the objectives will provide information on the role of salinity, temperature, condensate recovery, and inversion hysteresis of the conjugate emulsion phases for this chemical system. This information will be useful for incremental hydrocarbon recovery during the late period of the production of gas and gas condensate fields.

Presently work is in progress to characterize phase and emulsion behavior for ethylbenzene/water/ethanol system. During this reporting period, temperature scans were performed mixing equal volumes of ehtylbenzene and 10mM NaCl water with various concentrations of ethanol ranging from 2 to 70 vol%. For the range of temperatures tested (2 to 70 °C), results indicate that temperature is invariant and produced a single phase for ethanol concentrations greater than 60 vol%. For ethanol concentrations less than 60 vol%, only two phases were obtained with aqueous rich bottom phase more in volume than that of the ethylbenzene rich top phase. Linear coreflooding experiments were completed by our industrial partner in this project, Surtek, CO, to measure the ethylbenzene recovery in flooding processes. It was found about 30% ethylbenzene recovery was obtained by the waterflooding, however, 2 wt% ethanol flooding did not produce incremental recovery of the hydrocarbon. Radial coreflooding with ethanol injection prior to water injection is in progress to assess the effectiveness of the surfactant flooding in the recovery of ethylbenzene.

EXPERIMENTAL

Presently work is in progress to characterize phase, emulsion behavior, and condensate recovery for condensate/water/ethanol system.

Temperature scans were performed with 10 mm NaCl in water for various surfactant concentrations ranging from 2 to 70 vol% in tightly closed graduated glass bottles. Experiments were repeated for a range of temperatures from 2 to 70 EC. The small salt concentration was used to improve the sensitivity and accuracy of the conductivity measurements to be conducted in the next reporting period by increasing the conductivity differences between the conjugate phases of the emulsions. The best ethylbenzene/water/ethanol system defined by the above phase work will then be studied for emulsion morphologies. Briefly, electrical conductivities will be measured for top/bottom, and bottom/top phases that form the sides of the tie triangle diagram by mixing measured volumes of the pre-equilibrated phases.

Salinity scans that were conducted in the last reporting period were repeated to ascertain the number of phases formed. For this, equal volume of ethylbenzene and water with 10 vol% ethanol was mixed with various concentrations of NaCl ranging from 0 mM to 1000 mM. Each test mixture was kept in a graduated glass bottle with the lid-on this time to avoid evaporation of the mixture into the atmosphere. In the last reporting period, tests were conducted in open test tubes and during overnight settling of the phases, it was found a small quantity of the mixture was lost to the atmosphere by evaporation. The lost volume was assumed as that of the ethylbenzene rich top phase assuming the mixture produced three phases.

Core flooding measurements are being conducted by our industrial partner, Surtek, CO, to characterize condensate recovery. During this reporting period, linear corefloods were performed by injecting 2% surfactant (ethanol) dissolved in 10mM NaCl water into brine and ethylbenzene saturated core. Ethylbenzene recovery was determined by a mass balance and by modified Dean-Stark extraction of the core after the displacement studies. Effluent sample was analyzed for ethylbenzene recovery potential.

RESULTS AND DISCUSSION

Figures 1 and 2 present the results of the temperature scans at room temperature and 40 EC.. It can be seen that only two phases formed up to 60 vol% of the surfactant. It was also observed that the aqueous phase was more in volume than the condensate rich top phase. Experiments were repeated from 2 to 70 EC. Figure 3 presents the results of the temperature scans from 2 to 70 EC. It can be seen that above 60 vol% of the surfactant, the mixture produces single phase for the range of temperatures tested. It is concluded that temperature is invariant to this chemical system and produces more aqueous bottom phase than the condensate rich top phase.

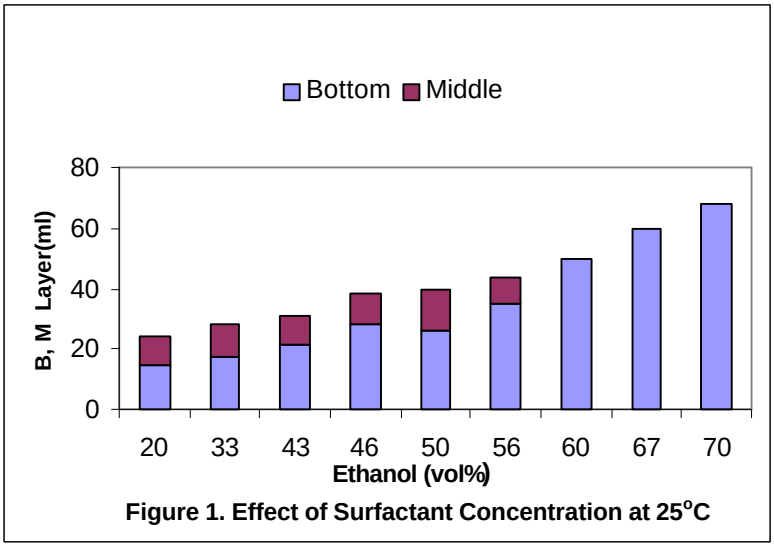

Figure 1. Effect of Surfactant Concentration at 25°C

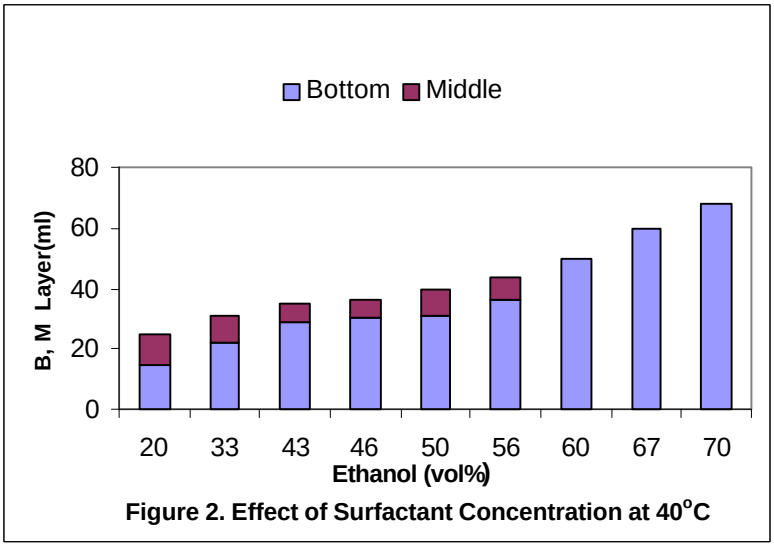

Figure 2. Effect of Surfactant Concentration at 40°C

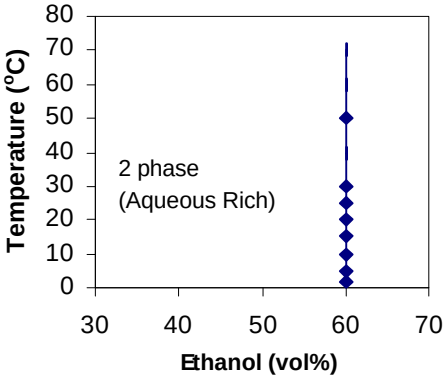

Figure 3. Temperature-Composition Cross Section of the Two Phase Region in the Ethylbenzene/Water/Ethanol System

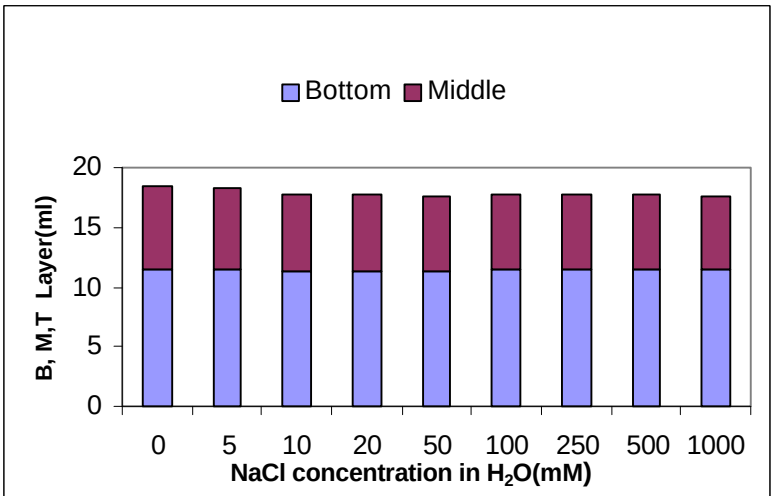

Figure 4. Salinity Scans at Ambient Temperature

Figure 4 presents the results of the salinity scans that were repeated in this reporting period at room temperature. It can be seen that indeed the mixture produces only two phases and incremental saline concentration does not make significant changes in the volume or number of the phases produced. Experiments were repeated at 30 EC and observed salinity has no effect at higher temperatures as well. It should be noted that Ross et al. [24] conducted phase studies for the mixture benzene-ethanol-water at 20 EC and observed two phases.

Results of the linear coreflooding experiment coducted by Surtek are as follows: A total of 30.8% of the original ethylbenzene saturation was recovered by injection of a 10mM NaCl solution. Injection of a 16 pore volume of 2% ethanol dissolved in 10 mM NaCl did not improve ethyl benzene recovery. Radial coreflooding experiments are in progress at Surtek. This time surfactant flooding will be carried out with a 100% ethanol solution prior to the water flooding to assess the effectiveness of the surfactant in ethylbenzene recovery.

Plans for the next Reporting Period

Setting up, testing, and calibration of the conductivity measurement system at Morehouse and Radial Corefloods at Surtek are expected to be completed within the next reporting period.

Outcome of this Period

Results presented here have been presented in a paper at the SPE/DOE Fourteenth Symposium on Improved Oil Recovery.

1) R. Sampath, L. Moeti, and H. McCulloch, "Salinity and Temperature Scans for Condensate/Water/Ethanol Mixtures," SPE/DOE Fourteenth Symposium on Improved Oil Recovery, April 20, 2004, Tulsa, OK.

CONCLUSION

The project is progressing well. Phase work including salinity and temperature scans were completed. Linear Coreflooding experiments were completed. Emulsion and Radial Coreflooding measurements are in progress.

ACKNOWLEDGMENTS

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REFERENCES

1. Duane H. Smith and K.-H. Lim, "Morphology and Inversions of Two Fluids in Systems of Three and Four Thermodynamic Dimension," J. Phys. Chem. 94, 3746-52 (1990).

2. Kunieda, H. and Friberg, S. E., Bull. Chem. Soc. Jpn. 1981, 54, 1010.

3. Duane H. Smith, "The Role of Critical Points in HLB and the Phase Inversion Temperature, Evidence from the Cyclohexane/ Water/ i-C9H19C6H4 (OCH2CH2)9.2OH--Temperature Trigonal Prismatic Diagram," J. Colloid Interface Sci. 108, 471 (1985).

4. Duane H. Smith, "Comparison of Emulsions with the Phase Diagrams of the Systems in which They Form" in Microemulsions, H.L. Rosano and M. Clausse, Eds. (Marcel Dekker, New York, 1987).

5. Duane H. Smith, Ramanathan Sampath, and Dady B. Dadyburjor, "Temperature-Dependent Inversion Hysteresis Lines for Emulsions of Middle and Bottom Phases of the System C6H13(OC2H4)2OH/n-Tetradecane/'Water'," J. Phys. Chem. 100, 17558-62 (1996).

6. Becher, P., J. Soc. Cosmetic Chem. 1958, 9, 141.

7. Duane H. Smith and K.-H. Lim, "An Experimental Test of Catastrophe and Critical-Scaling Theories of Emulsion Inversion," Langmuir 6, 1071 (1990).

8. Ross, S. and Kornbrekke, R. E., J. Colloid Interface Sci. 1981, 81, 58.

9. K.-H. Lim and Duane H. Smith, "Experimental Test of Catastrophe Theory in Polar Coordinates: Emulsion Inversion for the Ethanol/Benzene/ Water System," J. Colloid Interface Sci. 142, 278-90 (1991).

10. Duane H. Smith, G. L. Covatch, and K.-H. Lim, "Morphologies and Inversions of Emulsions of Conjugate Microemulsion and Oleic Phases in an Amphiphile/oil/Water System between Its Critical Endpoint Temperatures," Langmuir 7, 1585 (1991).

11. Clark, S.R., Pitts, M.J. and Smith, S.M.: "Design and Application of an Alkaline-Surfactant-Polymer Recovery System to the West Kiehl Field," (1993), SPE Advanced Technology Series, Vol 1, pages 172-179.

12. Manji, K.H. and Stasiuk, B.W.: "Design Considerations for Dome's David Alkali/Polymer Flood," Can. J. Pet. Tech., (May-June 1988), Vol. 27, pages 49-54.

13. Pitts, M.J., Surkalo, H. and Wyatt, K.: "Design and Field Implementation of Alkaline-Surfactant-Polymer Chemical Enhanced Oil Recovery Systems," proceedings of the 1995 UNITAR International Conference on Heavy Crude and Tar Sands, Houston, TX, Feb 12-16, 1995.

14. Lin, F.J., Besserer, G.J., and Pitts, M.J.: "Laboratory Evaluation of Cross-linked Polymer and Alkaline-Surfactant-Polymer Flood," (1987), Can. J. Pet. Tech., Vol. 35 (Nov.-Dec.).

15. Earlougher, R.C. Jr., O'Neal, J.E., and Surkalo, H.: Micellar Soltuion Flooding: Field Test Results and Process Improvements," SPE 5337, presented at the Rocky Mountain Regional Meeting, April 7-9, 1975.

16. Davis, J.A., Jr. and Jones, S.C.: "Displacement Mechanisms of Micellar Solutions," J. Pet. Tech., (Feb 1973), pages 186-194: Trans AIME, vol 243.

17. Sampath, R., Moeti, L., Smith, D., and Pitts, M., Characterization of Surfactants for Enhanced Oil Recovery, Technology Transfer Session, Historically Black Colleges/Universities and Other Minority Institutions Annual Symposium, April 28-29, 1998, Ocean City, MD.

18. Chen, J., Sampath, R., Moeti, L., and Smith, D., Salinity and Temperature Scans for a Novel AEC Surfactant, Technology Transfer Session, Historically Black Colleges/Universities and Other Minority Institutions Seventh Annual Symposium, April 1999, Miami, FL.

19. Chen, J., Sampath, R., Moeti, L., and Smith, D., Investigation of Phase and Emulsion Behavior for Novel Alcohol Ethoxycarboxylate Surfactants, Technology Transfer Session, Historically Black Colleges/Universities and Other Minority Institutions Annual Symposium, April 28-29, 1998, Ocean City, MD.

20. Johnson, G. K., A Study of Three-Phase Emulsion Behavior, PhD Dissertation, 1993, West Virginia University, Morgantown.

21. Duane H. Smith, G. K. Johnson, and D. Dadyburjor, "Continuous Phases in Emulsions of Three Liquids," Langmuir 9, 2089-92 (1993).

22. G. K. Johnson, D. Dadyburjor, and Duane H. Smith, "Electrical Conductivities of Three-Phase Emulsions. Part 2," Langmuir 10, 2523-27 (1994).

23. Duane H. Smith, G. K. Johnson, Y. C. Wang, and K.-H. Lim, "Electrical Conductivities of Three-Phase Emulsions. Part 1," Langmuir 10, 2516-22 (1994).

24. Sydney Ross, and Ralph E. Kornbrekke, “Change of Morphology of a Liquid-Liquid Dispersion as a Stochastic Process”, J. of Colloid and Interface Science, vol. 81, No. 1, 1981.